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Stability of cathode/electrolyte interfaces in high voltage Li-ion batteries

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Project ID # BAT331

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Overview

Timeline

- Start: October 2018
- End: September 2021
- 10%

Budget

- Total project funding
 - DOE share: 1.5M
- FY 18: \$500K
- FY 19: \$500K
- FY 20: \$500K

Barriers

- Barriers addressed
 - Stability
 - Ion transport
 - Efficiency

Partners

- Interactions/ collaborations
 - Zhengcheng Zhang

Solid-liquid Interfaces in Li-ion Batteries

General Objective

Develop fundamental mechanistic understanding of the principles that govern the decomposition and properties of cathode/electrolyte interfaces and relate them to the performance of high voltage Li-ion cells.

Strategy

Science-based approach - transfer of fundamental knowledge from model to real world systems.

Impact

Our goal is to help meet the high energy density demands of the new Li-ion technology are the high voltage Li-ion batteries, which utilize the cathode materials that can operate at voltages higher than 4.5 V vs. Li/Li⁺.

Aims relevant to next-generation lithium ion battery chemistries :

- Develop a methodology for the investigation of the degradation of cathode-electrolyte interfaces using fundamental science-based strategy.*
- Develop an in-depth understanding of degradation mechanisms of novel carbonate solvent-based electrolytes on well-defined model surfaces, followed by real cathode materials (NMC).*
- Studies will help to identify stable electrolyte/electrode interfacial components*

“Surface Science” Approach

Goal

To develop and use interdisciplinary, atomic-/molecular-level, insight obtained from integrating both experimental- and computational-based methodologies to define the landscape of parameters that control interfacial/bulk properties for Li-ion solid-liquid battery systems.

- ✓ Electrode-by-design strategy
- ✓ Electrolyte by design strategy

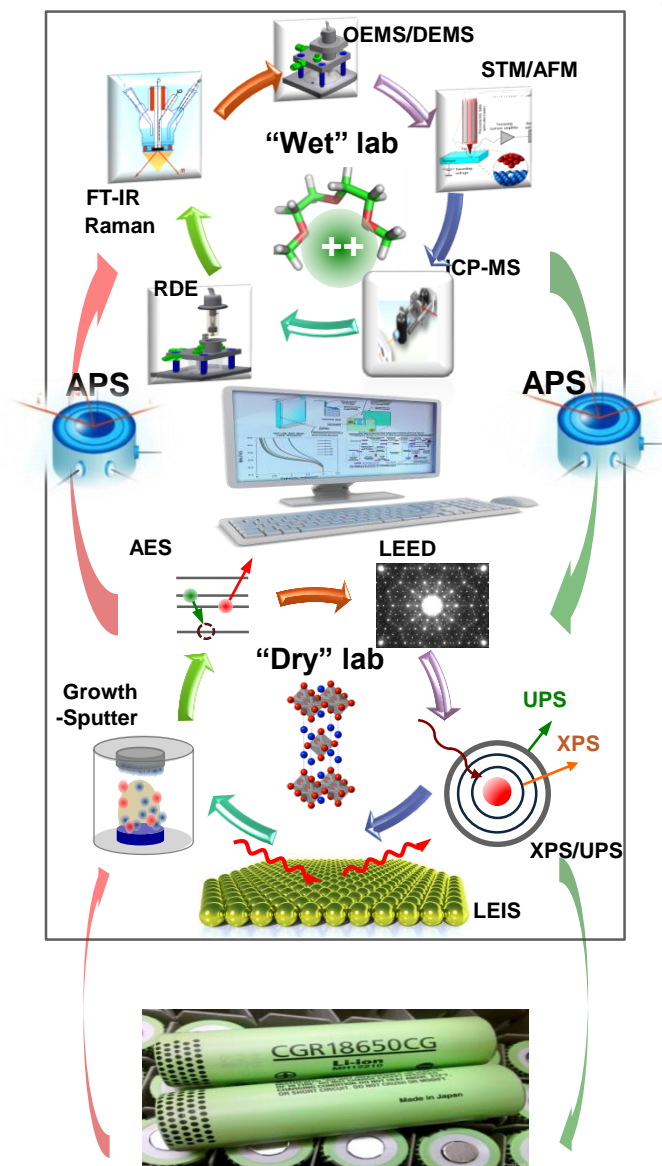
Syntheses methods

- ✓ Sputtering
- ✓ Pulse Laser Deposition
- ✓ High throughput modeling
- ✓ Solid Solution
- ✓ Chemical Vapor Deposition
- ✓ Electrochemical

Characterization methods

Various ex situ and in situ experimental tools and first principle-based modeling

- ✓ Low Energy Electron Diffraction
- ✓ X-Ray/Ultraviolet Photoel. Spect.
- ✓ Impedance
- ✓ DFT and molecular dynamics
- ✓ Fourier Transform Infrared Spectroscopy
- ✓ Differential Electroch.Mass Spectrometry/
- ✓ **Online Electrochemical Mass Spectrometry**
- ✓ Scanning Probe Microscopies
- ✓ Soft X-Ray Spectroscopy
- ✓ **Inductively coupled plasma mass spectrometry**



Science based Approach

Science-based approach - transfer of fundamental knowledge from model to real world systems.

- Investigate the chemistries of individual electrolyte components of a Li-ion battery on a variety of materials, from well-defined metal single crystals to realistic TMO samples at high potentials, relevant for high voltage LiB.*
- Investigate how the experimental conditions influence these individual chemistries or how they enhance or diminish individual processes in the case of overlapping chemistries.*
- By utilizing both theoretical as well as experimental tools, establish thermodynamic and kinetic windows of stability of individual components.*
- Combine the thermodynamic, kinetic and mass transport properties of a certain chemistry under specific experimental conditions to build an EEI with specific properties.*
- Test the performance of the EEI in coin cells.*

Milestones

Month/Year	Milestones
July/18	Develop procedures for preparation of model electrodes for RRDE including graphene samples with variable number of layers and miscut and thin film oxides.
August/18	Develop charging/discharging protocol to study decomposition of electrolyte on well defined model surfaces.
Sept/18	Develop approaches for studies of kinetic/thermodynamic stability windows for electrode/electrolyte systems using experimental and computational methods.
Oct/18	Develop ICP-MS technique for TMO dissolution including Co, Ni, Mn

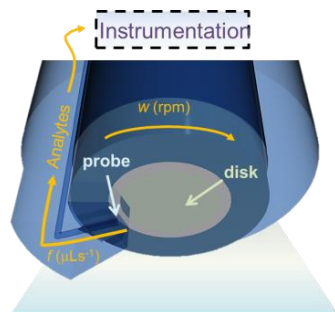


Preliminary Results

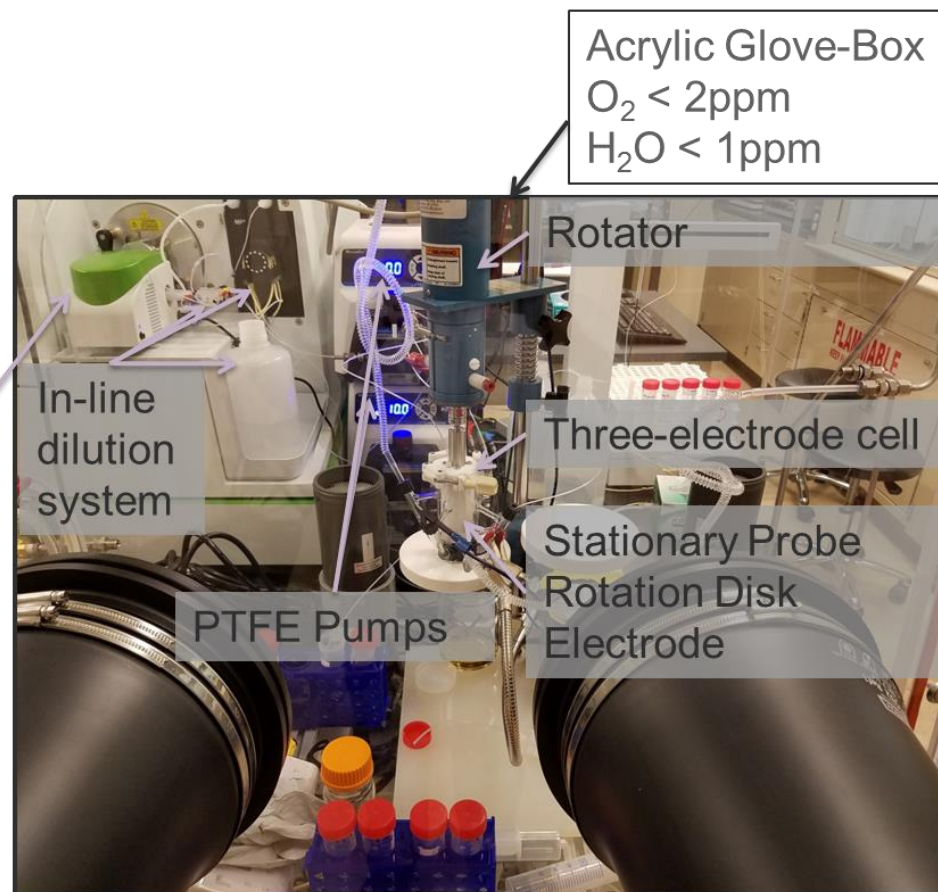
Measuring *in situ* dissolution of 3d elements

SPRDE-ICP-MS

- ✓ *In situ* dissolution allows independent determination of electrochemical currents and dissolution processes;
- ✓ High sensitivity of ICP-MS provides element-specific information with low detection limits to observe the early onset of dissolution processes;
- ✓ In turn, this provides information about failure mechanism;



ICP-MS
Temperature
Controlled
Sample
Introduction
System

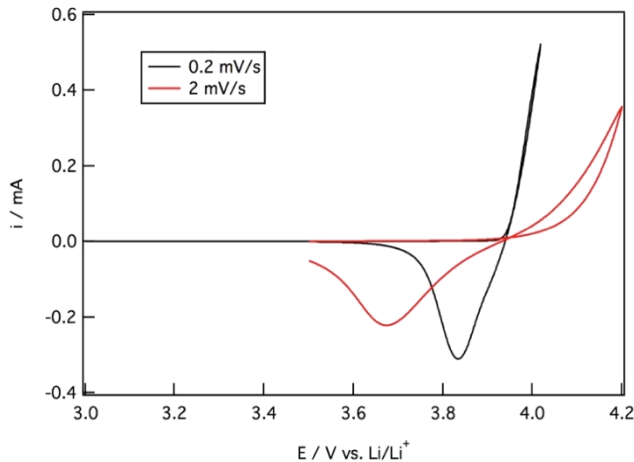


Concept



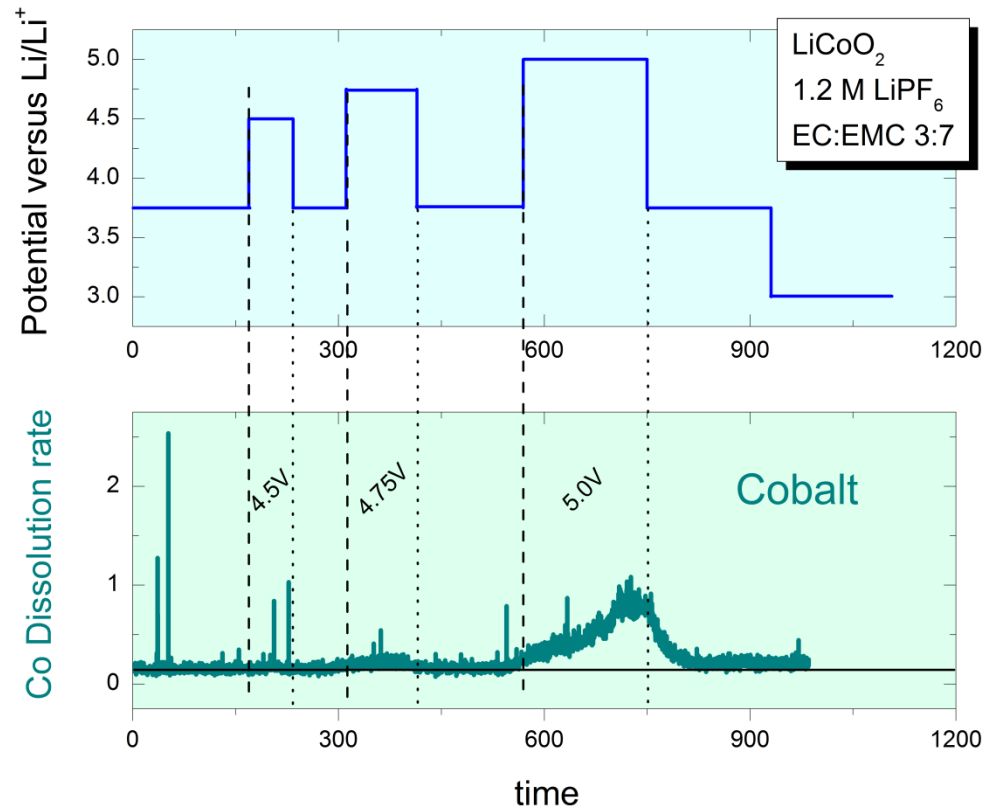
Reality

Benchmarking Cobalt dissolution from LiCoO_2



Typical cyclic voltammetry of charging and discharging LiCoO_2 in 1.2M LiPF_6 EC:EMC (3:7 by mass) electrolytes.

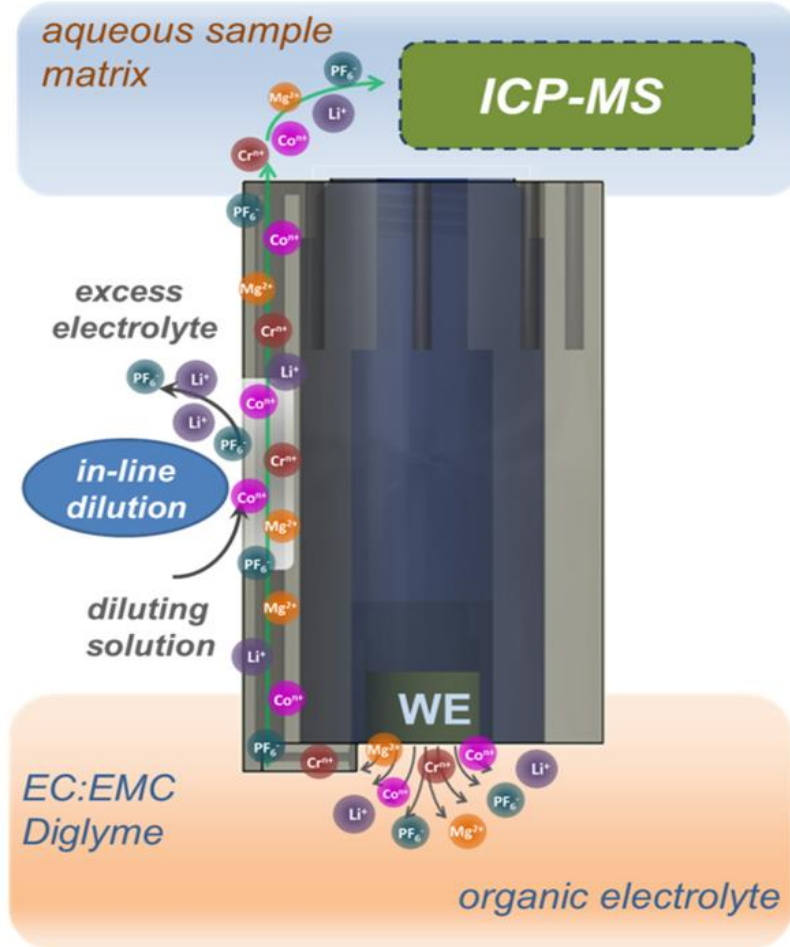
Distinct sweep rates highlights Li deintercalation/intercalation processes.



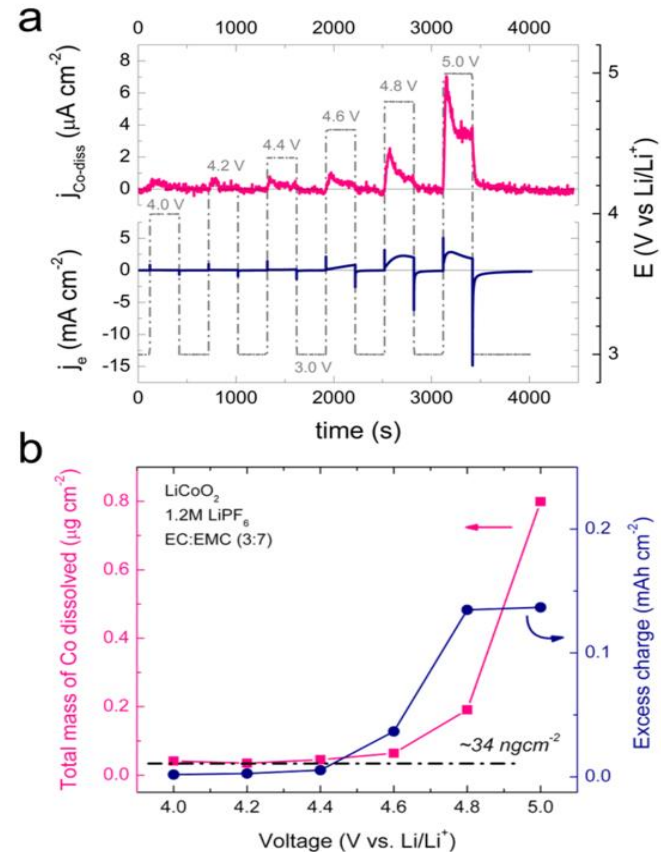
- Co dissolution measured above 4.5V, in agreement with coin cell experiments;
- Dissolution takes place well above deintercalation - confirming that is not tied to Li^+ removal from the structure.



Real-Time Monitoring of Cation Dissolution/De-Intercalation Kinetics from Transition Metal Oxides



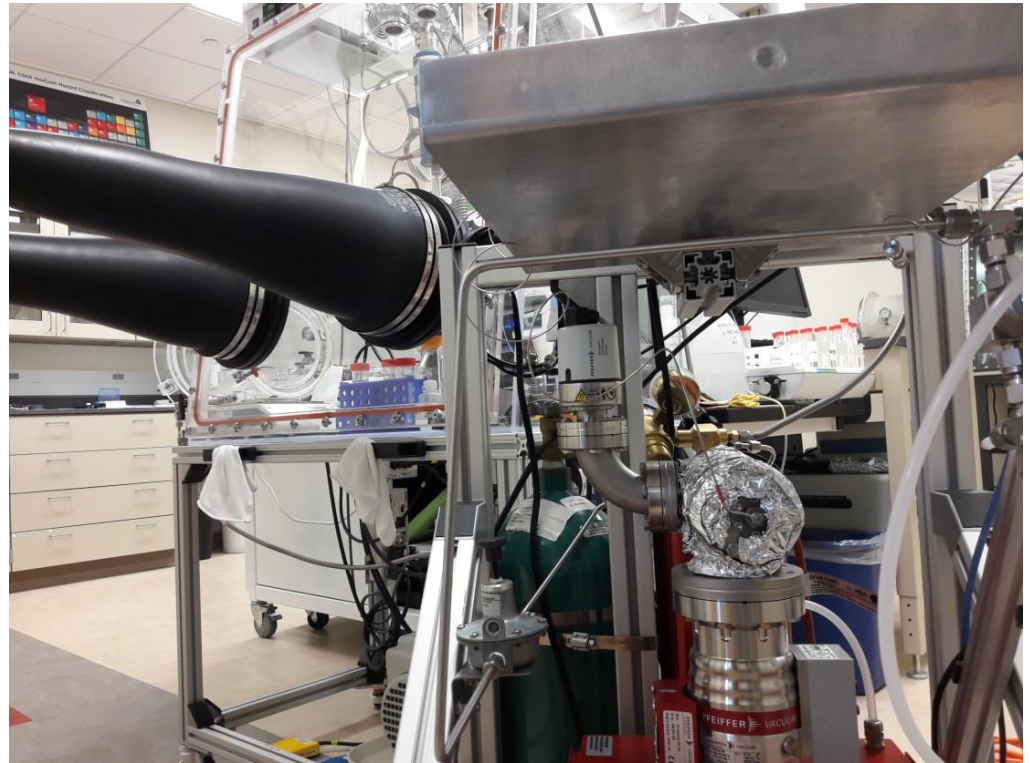
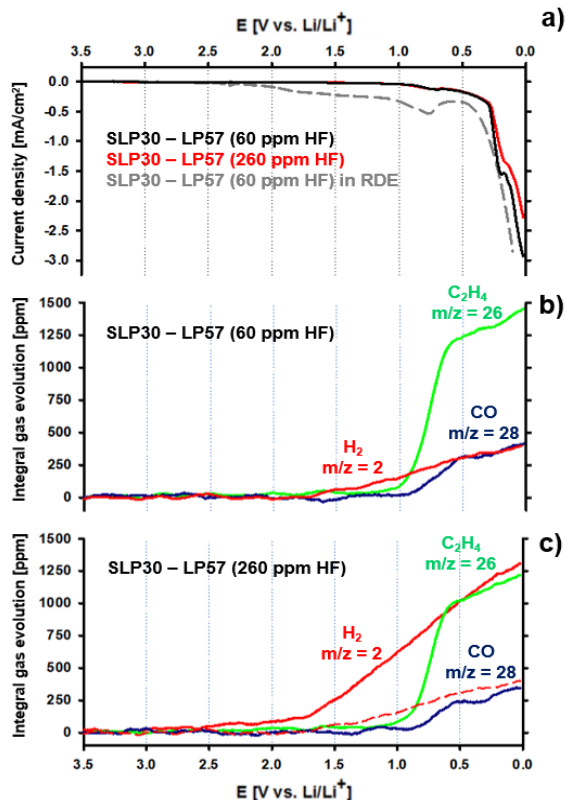
Schematic of the Stationary Probe Rotating Disk Electrode (SPRDE) system coupled to an Inductively Coupled Plasma Mass Spectrometry (ICP-MS)



a) *In situ* dissolution currents for Co ion dissolution (magenta) from LiCoO_2 in 1.2M LiPF_6 in 3:7 EC:EMC b) total mass of Co dissolved in each potential step window (left axis) and corresponding excess positive charge measured on the disk (right axis).

Preliminary results

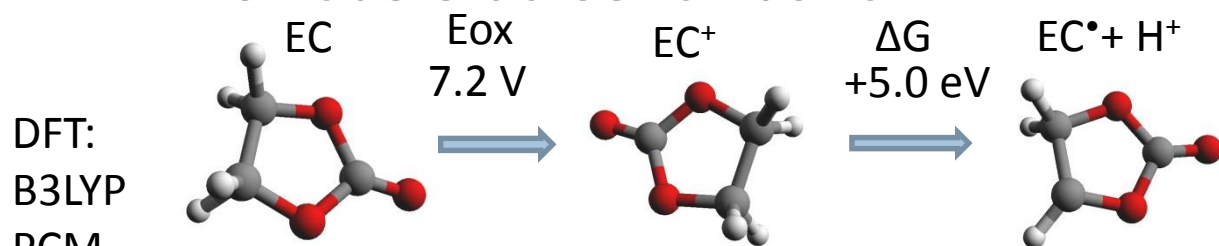
Measuring in situ gas evolution and electrolyte degradation: OEMS



a, Electrochemical response of SLP30 graphite in 1 M LiPF₆ in a real cell (black and red curves), and in the RDE configuration of our 3-electrode cell (grey curve) **b,c**, OEMS measurements of gas evolution from SLP30 graphite electrodes during scan in 1 M LiPF₆ containing 60 ppm HF (**b**) and 260 ppm HF (**c**).

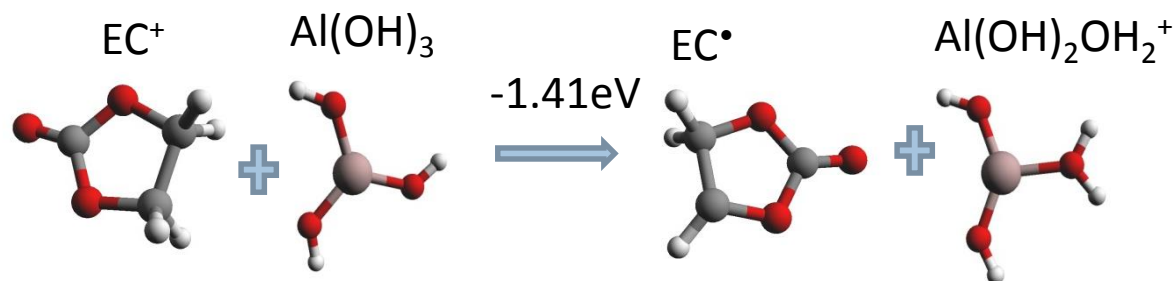
Computational studies: electrolyte/electrode reactivity

Previous studies: oxidation



EC becomes positively charged and then a proton is removed making it a radical: unfavorable

Previous studies: corrosion

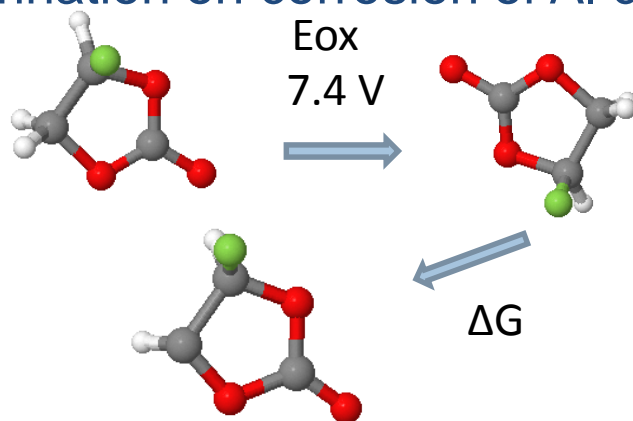


If the proton is transferred instead to an OH group coordinated to tetrahedral alumina, the second part becomes favorable

- Previous studies indicate lower oxidation potential in the presence of -OH or -SH groups coordinated to Al indicates feasibility of the proton transfer to alumina in the suggested corrosion mechanism for current collector.
- *Based on the previous electrolyte reactivity studies at oxide surfaces, we will explore reaction mechanisms relevant to electrolyte/electrode interface.*

Studies of stability of novel fluorinated electrolytes

Previous studies addressed the effect of electrolyte fluorination on corrosion of Al collector



Oxidation potential increases with the # of Fs, from 7.41 V for 1F to 8.21 V for 4F, but what about the H⁺ transfer?

- With increasing # of fluorines, oxidation is more difficult, however, in many cases, deprotonation is easier.
- Thus, increase in oxidation potential does not help to prevent Al corrosion in fluorinated electrolyte with 1F or 2F per EC.
- *This is a starting point for our studies of novel electrolytes that improve stability of electrode/electrolyte interface.*

Objectives:

1. *Investigate the chemistries of individual electrolyte components of a Li-ion battery on a variety of materials, from well-defined metal single crystals to realistic TMO samples at high potentials, relevant for high voltage LiB. These individual components will range from different solvents, electrolyte salts to possible impurities that can be either present in the electrolyte from the beginning or contaminate the system during battery operation (e.g. metals from the cathode side).*
2. *Investigate how the experimental conditions influence these individual chemistries or how they enhance or diminish individual processes in the case of overlapping chemistries.*
3. *By utilizing both theoretical as well as experimental tools, establish thermodynamic and kinetic windows of stability of individual components. Furthermore, an attempt will be made to include mass transport effects into the understanding of the interface stability in various electrochemical environments.*
4. *Combine the thermodynamic, kinetic and mass transport properties of a certain chemistry under specific experimental conditions to build an EEI with specific properties.*
5. *Test the performance of the EEI in coin cells.*

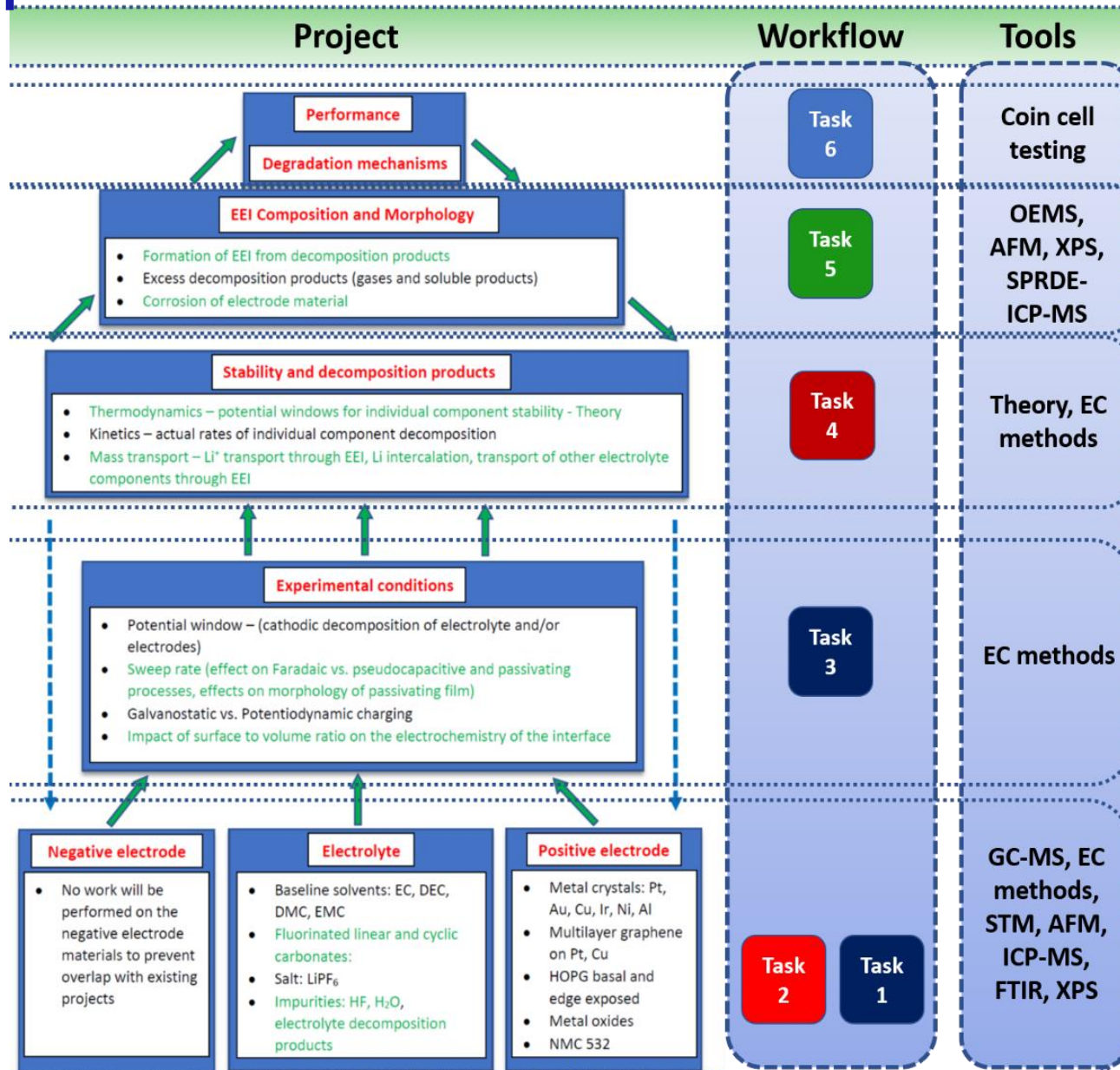


Proposed Future Work

Interconnected tasks:

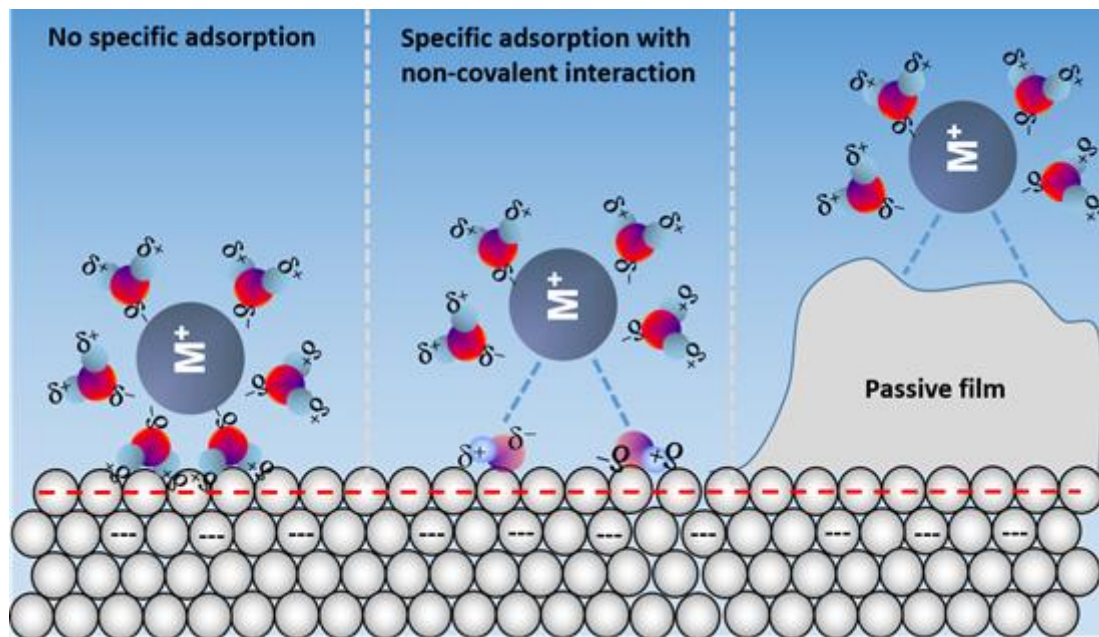
Task	Task title
Task 1	Exploring the chemistries of individual electrolyte components
Task 2	Development of model and realistic cathode materials for the investigation of specific processes at the cathode/electrolyte interface
Task 3	Role of experimental conditions on cathode/electrolyte degradation
Task 4	Stability and the decomposition products of electrolyte components
Task 5	EEL composition and morphology
Task 6	Performance

Proposed Future Work: Overview



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Proposed Future Work



These studies will address:

- How a specific interface will form upon contact of an electrode with an electrolyte: three types of interface.
- How the inhomogeneity of the interface along with transport phenomena of reacting species through the interface influence kinetics.
- What are thermodynamic/kinetic stability windows for electrolyte/electrode interface?

- By monitoring electrolyte reaction products and metal dissolution, investigate *in situ* kinetics of electrode degradation and EEI formation.
- By monitoring kinetics of complex metal oxide and electrolyte species, we will investigate mechanisms that determine the efficiency of the coin cell.

Response to last year reviewer's comments

New project, no reviewers' comments



Summary

- To date, there have been no methods able to provide quantitative, in situ information about the electrode dissolution kinetics and concomitant electrolyte decomposition during charge/discharge. Our novel approach enables simultaneous and independent measurements of transition metal cation dissolution rates from oxide hosts ($\text{Co}^{3+/4+}$) and de-intercalation kinetics of working cations and the relative rate of electrolyte decomposition.
- By developing fundamental mechanistic understanding of the principles that govern the decomposition and properties of cathode/electrolyte interfaces, we will help to improve the performance of high voltage Li-ion cells.